

Received December 12, 2014; reviewed; accepted March 30, 2015

LEACHING OF MANGANESE ORES USING CORNCOB AS REDUCTANT IN H₂SO₄ SOLUTION

Sajad ALI, Yaseen IQBAL, Umar FAROOQ, Sajjad AHMAD

Materials Research Laboratory, Department of Physics, University of Peshawar, Pakistan, Post code 25120 Pakistan, sajjad2485@yahoo.com

Abstract: In this study, corncob was used as reductant for sulfuric acid leaching of manganese ore from Daweezi, Upper Mohmand Agency, Pakistan. X-ray diffraction of representative powdered samples revealed the presence of manganese silicate MnSiO(SiO₄), calcite (CaCO₃), and α -quartz (SiO₂). X-ray diffraction and energy dispersive spectroscopy analyses indicated that the examined manganese ore was siliceous in nature. Three process parameters were investigated in the present study including the particle size of the ore, leaching temperature, and amount of corncob. Manganese extraction of 92.48 wt% was achieved for a leaching time of 60 min at 90 °C using 1.9 mol/dm³ H₂SO₄ concentration and 4 g of corncob. The present results demonstrated that corncob is a low cost, renewable, and non-hazardous reducing agent for manganese leaching under mild acid conditions in comparison to the other available reagents.

Keywords: *siliceous manganese ore, characterization, leaching, corncob, H₂SO₄*

Introduction

Manganese is an important element with several industrial applications such as steel, non-ferrous alloys, and paints production. Its non-metallurgical uses include fertilizers, animal feeds, colorants for bricks, textile dyes, and medicine (Pagnanelli et al., 2004). With increasing demand for manganese and gradual depletion of high grade manganese ore, various routes have been tried to develop an economical and efficient process to recover manganese from low-grade manganese dioxide ores (Haifeng et al., 2010). Low and medium-grade ores of manganese usually contain phosphorous, iron, and silica, rendering these ores unsuitable for usual industrial applications (Pagnanelli et al., 2004). Manganese occurs in nature mostly as pyrolusite (MnO₂) which is stable in acidic and alkaline media. Therefore, extraction of manganese from such a source has to be carried out under reducing conditions (Hariprasad et al., 2007). Low-grade of manganese dioxide ore can be treated by reductive acid leaching using different kinds

of reducing agents and acids (Pagnanelli et al., 2004). Coal is used as a reductant in traditional technology in order to convert manganese dioxide to manganese oxide which can be leached by sulfuric acid. This method produces smoke, dust, oxysulfide, and nitrogen oxides which greatly pollute the environment. Additionally, this method requires reaction temperature over 800 °C, which is too high for most of the reactors (Cheng et al., 2009).

Several other reducing agents have also been used traditionally under different acidic media e.g. pyrite, ferrous sulfate, aqueous sulfur dioxide, and hydrogen peroxide. Some of the reducing agents used as SO₂ may be harmful for the environment. Therefore, many investigators focused on reductive leaching of manganese dioxide ores using organic reductants mainly carbohydrates like glucose, sucrose, lactose, and oxalic acid. The use of organic reductant to leach manganese dioxide ores has been reported to be simple and efficient under mild temperature conditions (<90 °C) (Hariprasad et al., 2009), however the cost of reductant and high consumption rate limit the commercial applications of this technique (Tian et al., 2010).

Biomass can be used as a cheap and effective reductant to reduce manganese oxide ore at temperatures below 450 °C with a degree of reduction more than 95%. Moreover, as the amount of CO₂ released during the roasting process is equal to the amount absorbed during biomass growth, and this is a zero emission process for biomass fuel (Zhang et al., 2013). Adopting a zero-waste approach, carbohydrates from agriculture wastes are low-cost, renewable, and non-hazardous reducing agents that can be used for manganese leaching under mild acidic conditions (Lasheen et al., 2009). Among the biomass wastes, sawdust, cane molasses, corncob, cornstalks, rice husk, wheat stalks, bagass, bamboo, and shredded papers have been considered as environment-friendly and low-cost reducing agents for roasting reduction and leaching of manganese dioxide ore (Zhang et al., 2013). In order to extract manganese efficiently and economically by using waste materials, the hydrometallurgical treatment of low-grade manganese ore has attracted much attention in recent years (Chao et al., 2013).

In the present work, corncob was used as a reducing agent in a dilute sulfuric acid medium to extract manganese from siliceous manganese ores. In this process, corncob was hydrolyzed to release glucose under the acidic condition so that manganese dioxide could be reduced at a low temperature. The use of corncob for reduction of manganese dioxide is a simple, low cost, and economical method in comparison to the other available raw reductants. Using this method, manganese could be extracted up to about 90% (Tian et al., 2010).

Materials and methods

Manganese ore was obtained from Daweezi (34°35'60" N and 71°30'25" E), Upper Mohmand Agency, Khyber Pukhtunkhwa (KP), Pakistan. Semi-quantitative EDS

detected 60.7 wt% Mn, 15.8 wt% Ca, and 23.5 wt% Si in as-mined ore sieved through at 74 μm sieve. The ore was crushed, ground and passed through 149 and 74 μm sieves.

The leaching experiments were carried out in a 400 cm^3 glass beaker kept over a ceramic hot plate with magnetic stirring system in a fume hood. Initially 100 cm^3 concentrated H_2SO_4 (1.9 mol/dm^3) was mixed thoroughly with weighed amount of corncob (2, 3, and 4 g) to release the glucose into the acid. After 15 min, the weighed amount of ore (10 g) powder was transferred to the pulp. The leaching experiments were carried out for different sets of parameters i.e. different amounts of corncob, particles size, and temperatures.

Room temperature X-rays diffraction (XRD) data were recorded using a JEOL JDX-3532 X-ray diffractometer, operating at 40 kV and 30 mA, with Cu $K\alpha$ radiation ($\lambda \sim 0.154$ nm) at the Centralized Resource Laboratory (CRL), University of Peshawar, Pakistan. The samples were scanned from 10° - 70° (2θ) with a count time/step of 1.25 s and 0.02° step size. Secondary electron scanning electron microscope (SEM) images of chemically etched samples were recorded using a JEOL JSM5910 SEM, operating at 30 keV. Semi-quantitative energy dispersive X-ray electron (EDS) data were collected using an INCA200 EDS detector (Oxford instruments, UK) with analysis range from Boron to Uranium, connected with a JEOL-JSM5910 SEM. A PMG-3 microscope coupled with a DP-12 CCD camera, Olympus (Japan) was used for recording optical images in the present study at CRL.

Results and discussion

Characterization of as-mined samples

Figure 1a is a reflected light micrograph of chemically etched, finely polished manganese ore sample, showing the presence of three distinct micro-regions with different texture and morphology. The micro-regions with brownish golden contrast comprised anhedral grains (granular mineral with no definite morphology), marked as "A" (Fig. 1a), were manganese-rich (confirmed by SEM EDS). The jet-dark and cracked micro-regions, labeled as "B" (Fig. 1a), may also be rich in manganese as reported previously by Miaha et al. (2009). These micro-regions appeared as druses (crystals grown in a cavity, resulting in numerous crystal-tipped surfaces) and irregular in shape with no sharp boundaries/edges. The irregular cracks and slight alteration along the cracks are the characteristic features of manganese mineral. The apparently swelled grey regions marked as "C" (Fig. 1a) may be due to the effect of etching which could be seen in all the images of the chemically etched samples. The narrow black veins on the borders of the brownish gold color are also rich in manganese (Miaha et al., 2009). There were long zigzag cracks and veins in most of the micro-regions. However, some short and curved cracks were also seen.

Thin section study of the same sample showed two different textures that is one with dark and the other with bright contrast when viewed under the plane-polarized

light (Fig. 1b). Quartz appeared with bright contrast under plane polarized light and bright or grey when viewed under cross polarized light (MacKenzai et al., 1980). Iron was detected in veins and cracks as shown in Fig. 1b. The interlocked gangue mineral containing calcite or quartz was surrounded by manganese mineral with dark contrast. The micro-regions with bright contrast may be quartz or calcite as these minerals appear bright in plane polarized light (MacKenzai et al., 1980). Under plane polarized light the calcite shows granular texture and can be recognized by its good cleavage and twin lamellae.

The micro-regions with grey contrast in the cross polarized light photomicrograph (Fig. 1c) may be calcite with silica grains embedded in it (MacKenzai et al., 1980). The dark matrix may be the manganese-rich region. Mehdilo et al. (2013) reported the presence of bright and dark micro-regions in manganese ore under transmitted light microscope. The dark contrast was associated with the presence of manganese while the bright texture with calcite or quartz.

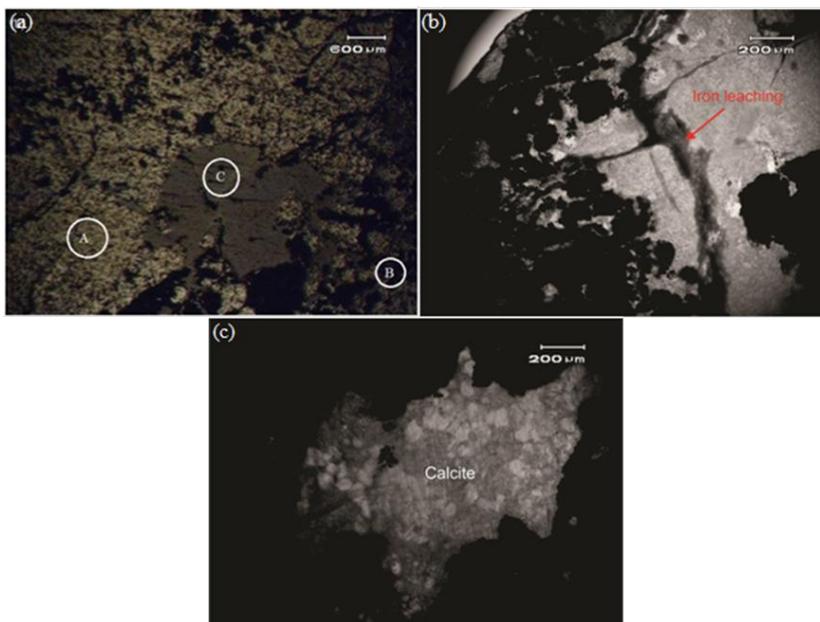


Fig. 1. a) Reflected light micrograph of as-mined Mn ore sample b) thin section view of Mn ore under plane polarized light c) thin section of the same sample under cross polarizer, showing various grains and micro-regions of varying contrast

Figure 2 shows room temperature XRD pattern recorded for as-mined manganese ore powder. The inter-planer spacings (d-values) and relative intensities corresponding to the major XRD peaks (labeled as ▼) matched PDF# 88-1232 for manganese silicate $MnSiO(SiO_4)$ indicating it to be the major phase in the examined sample. Additionally, some minor peaks matched PDF# 5-586 for calcite and PDF# 2-

458 for quartz showing these to be gangue minerals. A previous XRD study of manganese ore (Cheng et al., 2009) show the presence of pyrolusite (MnO_2) as the major phase along with small quantities of MgO , quartz (SiO_2), hematite (Fe_2O_3) and Al_2O_3 . Another XRD study (Su et al., 2008) of low-grade manganese ore from Bayi manganese mine, Guangxi, China reported the presence of todorokite ($\text{Mn}_6\text{O}_{12}\cdot 4.16\text{H}_2\text{O}$) and hematite (Fe_2O_3) as the major phases and quartz (SiO_2) and kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) as gangue minerals. Tian et al. (2010) also used XRD to investigate Hunan manganese ore, and reported the presence of a variety of metallic minerals including pyrolusite (MnO_2), todorokite ($\text{Mn}_6\text{O}_{12}\cdot 4.16\text{H}_2\text{O}$), goethite ($\text{Fe}_2\text{O}_3\cdot \text{H}_2\text{O}$), and gangue minerals consisting primarily of quartz (SiO_2), and kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$).

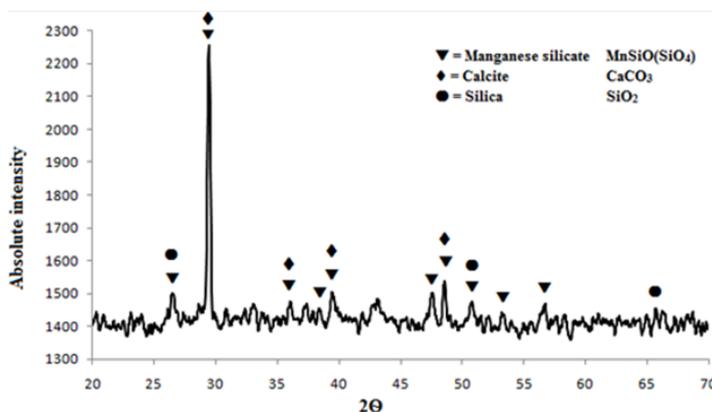


Fig. 2. XRD pattern of as-mined manganese ore showing peaks matching manganese silicate, calcite, and quartz

Figure 3 shows the secondary electron SEM images (SEIs) of as-mined manganese ore sample. EDS revealed that the irregular-shaped grains with light grey contrast marked as “A” were rich in manganese. The large grains with bright contrast and foggy surfaces “B” in Fig. 3 were calcium rich. EDS detected only Si in the relatively smaller grains with smooth surfaces marked as “C” which may be quartz. The gross elemental composition of the micro-regions shown in Fig. 3 is given in Table 1.

Table 1. Gross, white and light grey micro-regions composition of Fig. 3

Gross Composition		Bright Micro-region (B)		Light-grey Micro-region (A)	
Element	wt %	Element	wt %	Element	wt%
Mn	60.7	Mn	62.2	Mn	65.5
Ca	15.8	Ca	24.1	Ca	19.6
Si	23.5	Si	13.7	Si	14.9

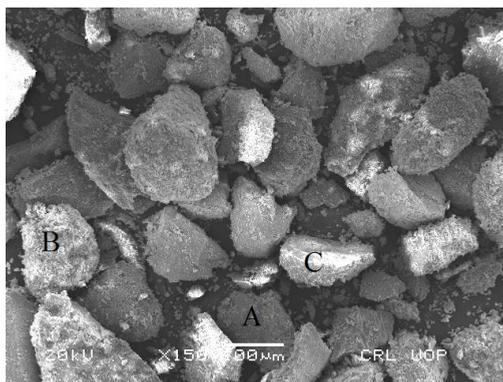


Fig. 3. SEI of as-mined manganese ore powdered sample sieved through 74 μm screen A and B show manganese-rich grains, and C shows silica-rich grain

Characterization of leached samples

Effect of particle size

EDS of the grains shown in Fig.4 (a-b) revealed an increase in manganese content from 51.8 wt.% to 76.4 wt.% by increasing particle size from 149 μm to 74 μm . The variation in elemental composition for 149 μm to 74 μm sizes is given in Table 2, and shown in Fig. 5.

The presence of sulfur observed in the leached manganese samples may be due to H_2SO_4 treatment of ore. Due to high density of manganese (7.35 g/cm^3), it settles down and calcium, silicon and sulfur cover the upper surface as evident from Fig. 4. EDS detected calcium and sulfur in the crushed grass-like features on the surface of the large grains of manganese with dark contrast. Table 3 shows the manganese extraction with different particle size.

Table 2. Elemental composition of 149 μm to 74 μm size sample

Size Fraction (μm)	Element Concentration (wt %)			
	Mn	Si	Ca	S
-149	51.8	21.5	2.1	----
-74	76.4	21.8	14.2	12.2

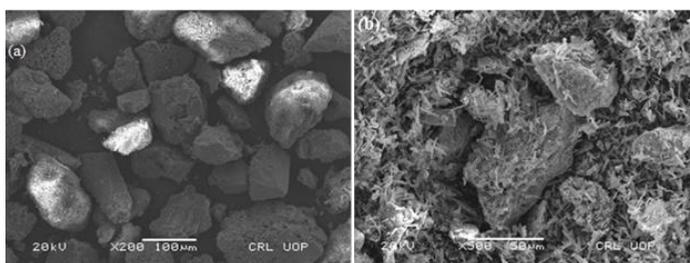


Fig. 4. SEI of processed sample through a) -149 μm particle size b) -74 μm particle size

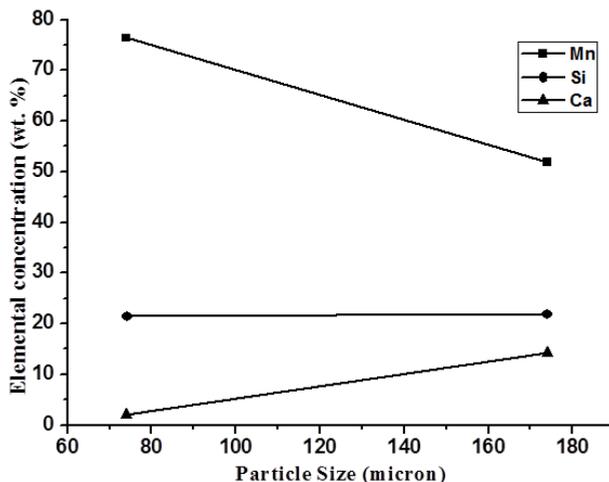


Fig. 5. Variation of elemental concentration with particle size

Table 3. Leaching results for 10 g of manganese ore treated with 3g of corncob for 60 min in 1.9 mol/dm³ of H₂SO₄ concentration at 90 °C for various particle sizes

Particle Size (μm)	Manganese Extraction (wt%)
-149	76.4
-74	51.80

Effect of corncob amount

Keeping the same concentration of sulfuric acid (i.e. 1.9 mol/dm³), leaching time of 60 min for 10 g of ore at 90 °C and particle size of 74 μm, the influence of corncob amount on leaching efficiency was investigated in detail. The variation in leaching efficiency of manganese ore and other elements with the amount of corncob are shown in Fig. 6. This experiment demonstrated that the leaching efficiency of manganese increased with the increase in the amount of corncob. The leaching efficiency of manganese increased up to ~92.5% when the amount of corncob was increased to ~4 g (Table 4). This was the highest leaching efficiency of manganese achieved in the present study. Therefore, 4 g of corncob was taken as the optimal parameter.

Table 4. Manganese extractions from its ore (-74 μm particle size) at 90 °C for a leaching time of 60 min in H₂SO₄ concentration of 1.9 mol/dm³ for various corncob amounts

Corncob Amount (g)	Manganese Extraction (wt%)
2	64.8
3	81.3
4	92.5

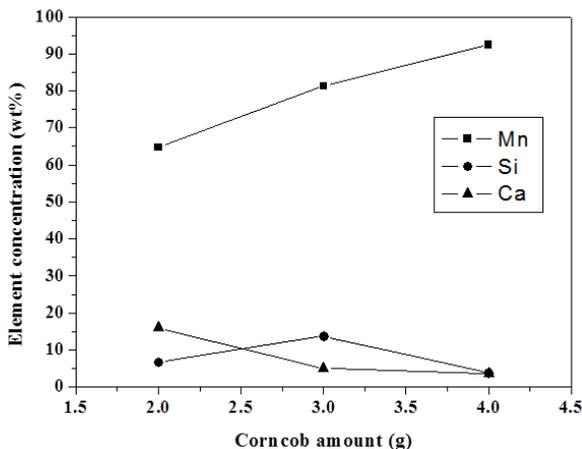


Fig. 6. Variation of chemical elements concentration with corncob amount

Effect of temperature

Table 5. Manganese extractions from its ore treated with 3 g corncob, 60 min of leaching time, H_2SO_4 concentration of 1.9 mol/dm^3 , particle size of $74 \mu\text{m}$ for various temperatures

Temperature ($^{\circ}\text{C}$)	Manganese Extraction (wt%)
70	58.39
100	81.20

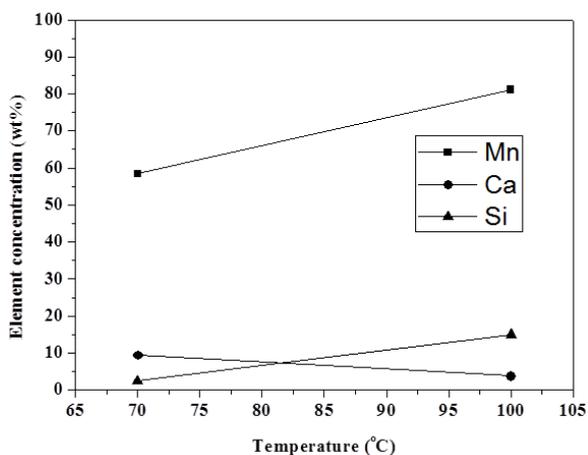


Fig. 7. Variation of chemical elements concentration with temperature

Keeping the corncob amount fixed at 4 g, sulfuric acid concentration at 1.9 mol/dm^3 , leaching time of 60 min, ore amount of 10 g and particle size of $74 \mu\text{m}$, the influence of temperature on leaching efficiency was investigated. Two leaching experiments were carried out at 70°C and 100°C . The result obtained is given in Fig.

7 showing variation of elemental concentration with temperature. It is observed that by increasing the temperature from 70 °C to 100 °C, manganese recovery after 60 min leaching increased from 58.39% to 81.20%. In this study, the most favorable leaching temperature was 100 °C (Table 5).

Conclusion

In this study, a manganese ore from Daweezi (Mohmand Agency, Pakistan) was characterized using optical microscopy, XRD, SEM and EDS techniques. The Daweezi manganese ore is a high-grade siliceous manganese ore. The mineralogical constituents of the ore are manganese silicate [$\text{MnSiO}(\text{SiO}_4)$], calcite (CaCO_3) and α -quartz (SiO_2). Manganese ore was upgraded by acid reductive leaching using predetermined concentration of H_2SO_4 in the presence of corncob as reductant. The investigated factors were temperature, particle size and corncob amount. The best operating conditions giving the highest manganese content were 90 °C, 74 μm size, leaching time of 60 min, H_2SO_4 concentration of 1.9 mol/dm^3 and 4 g corncob. The present results indicated that with the variation of temperature the rate of leaching efficiency increased. Manganese extraction from manganese ore strongly depends on the reaction temperature. With the decrease of ore particle size, the manganese recovery increased. With the increase of corncob amount the manganese extraction increased while the silica concentration decreased. Considering that the process productively use corncob from the environment, the technology should be beneficial from both economic and environmental perspective.

Acknowledgment

The authors acknowledge the financial support of the Higher Education Commission (HEC) for Pakistan, the US National Academy of Science under the Pak-US S&T Cooperation Program, Materials Research Laboratory (MRL) and Centralized Resource Laboratory (CRL) University of Peshawar, Pakistan.

References

- CHENG, Z., ZHU, G., ZHAO, Y., 2009, *Study in reduction–roast leaching manganese from low-grade manganese dioxide ores using cornstalk as reductant*, Hydrometallurgy, 96, 176-179.
- CHAO, X., LONGJUN, X., TIEFENG, P., KUN, C., JING, Z., 2013, *Leaching process and kinetics of manganese in low- grade manganese ore*, Chinese Journal of Geochemistry, 32, 222-226.
- HARIPRASAD, D., DASH, B., GHOSH, M.K., ANAND, S., 2007, *Leaching of manganese ores using sawdust as a reductant*, Minerals Engineering, 20, 1293-1295.
- HARIPRASAD, D., DASH, B., GHOSH, M.K., ANAND, S., 2009, *Mn recovery from medium grade ore using a waste cellulosic reductant*, Indian Journal of Chemical Technology, 16, 322-327.
- HAI FENG, S., HUAIKUN, L., FAN, W., XIAOYAN, L., YANXUAN, W., 2010, *Kinetics of reductive leaching of low-grade pyrolusite with molasses alcohol wastewater in H_2SO_4* , Chinese Journal of Chemical engineering, 18(5), 730-735.

- LASHEEN, T.A., EL-HAZEK, M.N., HELAL, A.S., EL-NAGAR, W., 2009, *Recovery of manganese using molasses as reductant in nitric acid solution*, International Journal of Mineral Processing, 92, 109-114.
- MACKENZAI, W.S., GUILFORD, C., 1980, *Atlas of Rock-forming Minerals in Thin Sections*, Longman Scientific & Technical, 89-90.
- MIAHA, P.P., MOHAPATARA, B.K., MAHANTA, K., 2009, *Upgradation of low-grade siliceous manganese ore from Bonai-Keonjhar belt, Orissa*, Indian Journal. Minerals and Materials Characterization and Engineering, 8(1), 47-56.
- MEHDILO, A., IRANNAJAD, M., HOJJATI-RAD, M.R., 2013, *Characterization and beneficiation of Iranian low grade manganese ore*, Physicochemical Problems of Mineral Processing, 49(2), 725-741.
- PAGNANELLI, F., FURLANI, G., VALENTINI, P., VEGLIO, F., TORO, L., 2004, *Leaching of low-grade manganese ores by using nitric acid and glucose: optimization of the operating conditions*, Hydrometallurgy, 75, 157-167.
- SU, H., WEN, Y., WANG, F., SUN, Y., TONG, Z., 2008, *Reductive leaching of manganese from low-grade manganese ore in H_2SO_4 using cane molasses as reductant*, Hydrometallurgy, 93,136-139.
- TIAN, X., WEN, X., YANG, C., LIANG, Y., PI, Z., WANG, Y., 2010, *Reductive leaching of manganese from low-grade manganese dioxide ores using corncob as reductant in sulfuric acid solution*, Hydrometallurgy, 100, 157-160.
- ZHANG, H., ZHU, G., YAN, H., LI, T., ZHAO, Y., 2013, *The mechanism on biomass reduction of low-grade manganese dioxide ore*, *The Minerals, Metals and Materials Society and ASM International*.
- ZHANG, H., ZHU, G., YAN, H., ZHAO, Y., LI, T., FENG, X., 2013, *Reduction of low-grade manganese dioxide ore pellets by biomass wheat stalk*, Acta Metallurgica Sinica, 26 (2), 167-172.